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(19) (CA) **CANADIAN PATENT** (12)

(54) Obtaining Anhydrous or Substantially Anhydrous Formic Acid by Hydrolysis of Methyl Formate

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Canada

Obtaining anhydrous or substantially anhydrous formic acid by hydrolysis of methyl formate

The present invention relates to a process for obtaining anhydrous or substantially anhydrous formic acid by hydrolysis of methyl formate. The production of anhydrous formic acid by hydrolysis of methyl formate has been described in several publications in the patent literature, for example in German Laid-Open Applications DOS 2,744,313, DOS 2,853,991 and DOS 2,914,671.

For example, German Laid-Open Application DOS 2,744,313 discloses that the hydrolysis of the methyl formate can be carried out in the presence of an organic base, eg. 1-pentylimidazole, an adduct of formic acid with the particular base being formed. The remaining reactants are first separated from the adduct and the formic acid is then separated from the base, these operations being carried out in two separate distillation stages taking place in succession. The disadvantage of this process is that the cleavage of the formic acid from the adduct requires severe distillation conditions, under which both the formic acid and the base begin to decompose.

This disadvantage is avoided by the processes described in German Laid-Open Applications DOS 2,853,991 and DOS 2,914,671. In these processes, the components methanol and methyl formate are first distilled off, at the top, from the mixture of substances obtained in the hydrolysis of the methyl formate, and the bottom product consisting of formic acid and water is fed to a liquid-liquid extraction with an extracting agent which mainly takes up the formic acid. First the water and then the formic acid are subsequently distilled off from the extract phase in two separate steps, without significant decomposition reactions taking place, as are observed in the procedure described in German Laid-Open Application DOS 2,744,313. In contrast to this laid-open application, however, the processes described in German Laid-Open Applications DOS 2,853,991 and DOS 2,914,671 employ a

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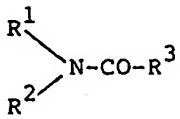
liquid-phase extraction in order to separate off the water.

It is an object of the present invention to provide an economical process for obtaining anhydrous or substantially anhydrous formic acid, the process being free of troublesome decomposition reactions and not requiring a liquid-liquid extraction for separating off the unreacted water from the methyl formate hydrolysis.

We have found that this object is achieved, in accordance with the invention, by a process for obtaining anhydrous or substantially anhydrous formic acid by hydrolysis of methyl formate wherein

a) methyl formate is hydrolyzed in the presence of a carboxamide of the general formula (I):



(I)

where R^1 is alkyl or hydrogen, R^2 is alkyl, R^3 is hydrogen or a C_1 to C_4 alkyl, and R^1 and R^2 may form part of a 5-membered or 6-membered ring, and the sum of the carbon atoms in the radicals R^1, R^2 and R^3 is from 1 to 14,

b) a mixture formed during the hydrolysis is separated into its individual components in a 1st distillation column which is divided into a feed part and a take-off part by separating means which are effective in the longitudinal direction,

- the hydrolysis mixture being fed into the feed part,
- methanol and unreacted methyl formate being taken off as a top product and as a side product,
- formic acid and the carboxamide of the formula I, as an extracting agent, being taken off as an anhydrous or substantially anhydrous bottom product, and
- water, preferably in liquid form, being removed from the

take-off part, and

c) the bottom product from the 1st distillation column is separated, in a 2nd distillation column, into formic acid and the extracting agent.

The carboxamide of the formula I may be a formamide which does not form an azeotropic mixture with formic acid. The carboxamides used may be N,N-di-n-propylformamide and/or N,N-di-n-butylformamide. When R^1 and R^2 form part of a five or six-membered ring, it is preferred that the ring be either piperidine or pyrolidine. Carboxamides where the sum of the carbon atoms in R^1, R^2 and R^3 is from 1 to 6, are preferred.

To improve the separating power of the 1st distillation column it was found to be advantageous if an aditional amount of the carboxamide was fed into the 1st distillation column, above the feed point for the hydrolysis mixture and below the take-off point for the water.

The feed part and the take-off part of the 1st distillation column may consist of 2 distillation columns arranged separately side by side. It is also possible for the take-off part to be in the form of a rectifying column or a stripping column.

The core of the present invention, and critical with regard to the cost-efficiency of the process, is the use of the 1st distillation column divided in the longitudinal direction, which makes it possible to remove the unreacted water from the methyl formate hydrolysis in liquid or vapor form, preferably in liquid form, and substantially free of formic acid. Hence, the heat of condensation of the water separated off is utilized for the

separation of substances in the distillation column. Compared with the processes described in German Laid-Open Applications DOS 2,853,991 and DOS 2,914,671, the novel process has the advantage that the completely water-miscible carboxamides, too, can be used in the dehydration of the formic acid by distillation, these carboxamides having a fairly low boiling point in some cases and hence permitting simpler and more economical separation of the formic acid from the extracting agent in the 2nd distillation column. Another advantage of the novel process is that the extracting agent is already present in the reacted mixture, and re-esterification in the course of the methanol/methyl formate separation is thus substantially suppressed. An example of the invention is shown in the drawing and is described in detail below. The drawing shows a flow diagram of the process according to the invention.

The experimental plant consisted of a reactor 1 for carrying out the hydrolysis and two distillation columns 2 and 3 for separating the hydrolysis mixture formed in the reaction into its individual components. The reactor used was a stirred vessel having a reaction space of 0.8 l, the reaction being carried out at about 150°C and under about 10 bar. The reactor was charged with the fresh feeds 7, consisting of 180 g/h of methyl formate

with an additional 5 g/h of methanol, and 55.5 g/h of water. Furthermore, the top product 5 from the 1st distillation column, consisting of 244 g/h of methyl formate and 13 g/h of methanol, the lower sidestream 6 from the 1st distillation column, consisting of 72.5 g/h of water, 4.5 g/h of formic acid, 1 g/h of di-n-butylformamide and 6 g/h of methanol, and the bottom product 4 from the 2nd distillation column, consisting of 657 g/h of di-n-butylformamide and 1 g/h of formic acid, were fed to the reactor. The residence time in the reactor was about 30 minutes. The hydrolysis mixture which was obtained as a liquid reaction product 8 and consisted of 254 g/h of methyl formate, 115 g/h of methanol, 135.5 g/h of formic acid, 77 g/h of water and 658 g/h of di-n-butylformamide was fed into the 1st distillation column at the middle of the feed part. In addition to the abovementioned amounts of top product and sidestream 6 from the 1st distillation column, 125.5 g/h of formic acid, 657 g/h of di-n-butylformamide and 6.5 g/h of water were removed as a bottom product 9 from this distillation column and fed to the 2nd distillation column. 92 g/h of methanol and 17.5 g/h of methyl formate were taken off in liquid form, as a further sidestream 10 from the 1st distillation column. In addition to the abovementioned bottom product 4, the desired end product was obtained from the 2nd distillation column as a top product 11 in an amount of 124.5 g/h of formic acid and 6.5 g/h of water, the di-n-butylformamide content being below 5 ppm.

The 1st distillation column was operated under atmospheric pressure, had an internal diameter of 50 mm and contained packing which was 4,000 mm high and consisted of glass Raschig rings having a diameter of 5 mm. The height of the packing corresponded to 50 theoretical plates. Between the 5th and the 20th theoretical plates, the distillation column was divided, by means of a glass plate, into 2 sections, both having the same cross-section, so that cross-mixing of liquid streams and vapor streams

was prevented in this region of the distillation column. The point at which the reaction mixture 8 was fed into the distillation column was located in the middle of the feed part, ie. at the height of the 13th theoretical plate, while the take-off point for the sidestream 6 was located exactly opposite, at the same height, in the take-off part. The sidestream 10 was removed at the level of the 43rd theoretical plate. The temperature profile within the distillation column was as follows: 32°C at the top, 53°C at the 43rd theoretical plate, 96°C at the 13th theoretical plate in the take-off part, and 162°C at the bottom. The reflux ratio was 1.0. At the upper end of the longitudinal division, the liquid was divided between the take-off part and the feed part in a ratio of 7.3 : 1.

The 2nd distillation column was operated at a top pressure of 80 mbar and with a reflux ratio of 1.6, and the number of separating stages corresponded to 20 theoretical plates. The temperature at the top of the distillation column was 37°C, while that at the bottom was 159°C.

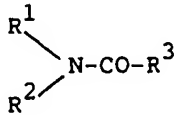
To improve the separating power of the 1st distillation column, it was found to be advantageous if 100 g/h of di-n-butylformamide were fed in above the feed point (about 3 theoretical plates higher) and below the side take-off point (about 3 theoretical plates lower) in the longitudinally divided section of the distillation column. (These amounts are not taken into account in the above balance of amounts.)

In a further embodiment of the apparatus for the novel process, instead of a distillation column which has in the middle section a separating means which is effective in the longitudinal direction, a column system is used in which the feed part and the take-off part are in the form of distillation columns arranged side by side. It is also possible for the take-off part to be in the form of a rectifying column or a stripping column.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for obtaining anhydrous or substantially anhydrous formic acid by hydrolysis of methyl formate, wherein

a) methyl formate is hydrolyzed in the presence of a carboxamide of the general formula (I):



(I)

where R^1 is alkyl or hydrogen, R^2 is alkyl, R^3 is hydrogen or a C_1 to C_4 alkyl, and R^1 and R^2 may form part of a 5-membered or 6-membered ring, and the sum of the carbon atoms in the radicals R^1, R^2 and R^3 is from 1 to 14,

b) a mixture formed during the hydrolysis is separated into its individual components in a 1st distillation column which is divided into a feed part and a take-off part by separating means which are effective in the longitudinal direction,

- the hydrolysis mixture being fed into the feed part,
- methanol and unreacted methyl formate being taken off as a top product and as a side product,
- formic acid and the carboxamide of the formula I, as an extracting agent, being taken off as an anhydrous or substantially anhydrous bottom product, and
- water being removed from the take-off part, and

c) the bottom product from the 1st distillation column is separated, in a 2nd distillation column, into formic acid and the extracting agent.

2. A process according to claim 1, wherein the water is removed in liquid form.

3. A process according to claim 1, wherein a formamide which does not form an azeotropic mixture with formic acid is used as the carboxamide of the formula I.

4. A process according to claim 1, wherein the carboxamides used are N,N-di-n-propylformamide and/or N,N-di-n-butylformamide.

5. A process according to claim 1, wherein an additional amount of the carboxamide is fed into the 1st distillation column, above the feed point for the hydrolysis mixture and below the take-off point for the water.

6. A process according to claim 1, wherein the feed part and the take-off part of the 1st distillation column consist of 2 distillation columns arranged separately side by side.

7. A process according to claim 6, wherein the separate take-off part consists only of a rectifying column at whose upper end the water to be recycled is condensed in a heat exchanger and removed in liquid form, and the heat of condensation evolved is used for vaporising liquid from the main column.

8. A process according to claim 6, wherein the separate take-off part consists only of a stripping column whose lower end is heated with vapors from the main column, and from which the water to be recycled is taken off as a bottom product in liquid form.

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9. A process according to claim 1, wherein R^1 and R^2 together form part of a piperidine or pyrrolidine ring.

10. A process according to claim 1, wherein the sum of the carbon atoms in the radicals R^1, R^2 and R^3 is from 1 to 6.

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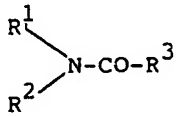
ABSTRACT OF THE DISCLOSURE:

Anhydrous of substantially anhydrous formic acid is obtained by hydrolysis of methyl formate by a process in which, methyl formate is hydrolyzed in the presence of a carboxamide of the general formula (I):



(I)

where R^1 is alkyl or hydrogen, R^2 is alkyl, R^3 is hydrogen or a C_1 to C_4 alkyl, and R^1 and R^2 may form part of a 5-membered or 6-membered ring, and the sum of the carbon atoms in the radicals R^1, R^2 and R^3 is from 1 to 14. The mixture formed during the hydrolysis is separated into its individual components in a first distillation column which is divided into a feed part and a take-off part by separating means which are effective in the longitudinal direction. During the process the hydrolysis mixture is fed into the feed part, while methanol and unreacted methyl formate are taken off as a top product and as a side product. Formic acid and the carboxamide of formula I (as extracting agent) are taken off as an anhydrous or substantially anhydrous bottom product. Water, preferably in liquid form, is removed from the take-off part. Finally the bottom product from the first distillation column is separated, in a second distillation column, into formic acid and the extracting agent. This process avoids decomposition of the products and does not require liquid-liquid extraction to remove water.

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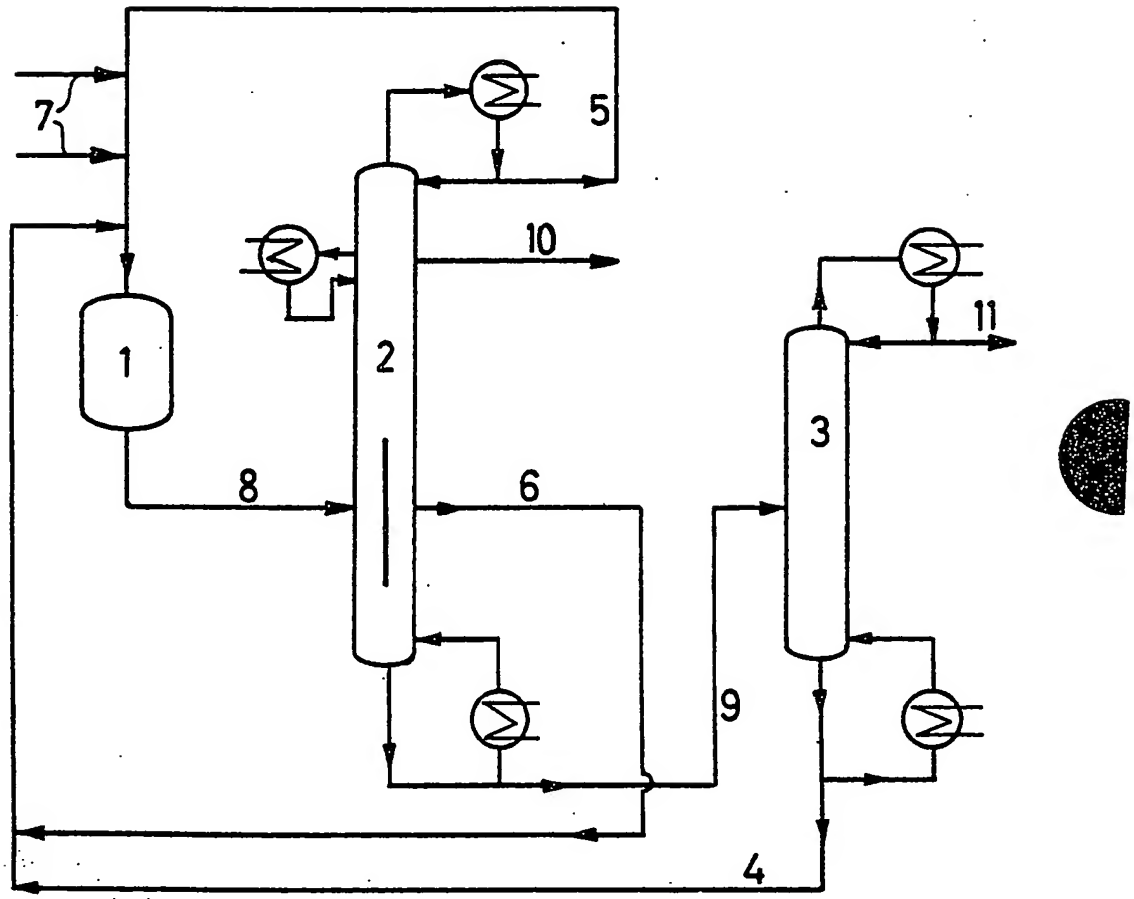

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